Investigating the Application of the Separation Capabilities of a Zirconium MOF β-oriented MFI Zeolite Membrane

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Abstract

Many people from third world countries still lack access to clean and safe drinking water, leading to a rise in water borne diseases like cholera. This project investigated the water purification capabilities of the Zirconium MOF β-oriented MFI Zeolite Membrane in comparison with the commercial α- alumina membrane with the aim of improving the purification capabilities of these membranes. The following tests were carried out to investigate the separation capabilities of the membranes in terms of NaCl, copper(II) ions and zinc ions respectively. In the NaCl separation tests, the zirconium membrane removed 43.1% of NaCl from water, whereas the α- alumina membrane only managed to remove 18.7% of NaCl; for copper(II) ions, the percentage removal for the α- alumina membrane and zirconium membrane were 14.3% and 63.3% respectively; for zinc ions, the percentage removal were 36.9% and 37.3% respectively. The Zirconium membrane showed promising results compared to the α- alumina membrane in most aspects and showed great potential in water purification.

1. Introduction

According to water.org, 785 million people – 1 in 9 people – lack access to safe drinking water. This has led to the spread of waterborne diseases where there are more than 3.4 million deaths from waterborne diseases every year, making it the leading cause of disease and death around the world (Hawthorne, 2019). Desalination, a water purification technique, is a reliable method for obtaining clean water from seawater, thus increasing the availability of clean, safe drinking water. Desalination removes the NaCl and minerals from seawater, making it no longer saline and suitable for consumption. There has been an exponential growth of desalination over the years as it has been shown to be a cheap and effective method of obtaining safe and clean drinking water. Desalination requires reverse osmosis and a nanoporous membrane is needed. More effective and efficient membranes are hence important.

The reason why a zirconium membrane was chosen as the test membrane was because zeolite membranes demonstrate promising separation performance that make them potential membrane candidates in water desalination and heavy metal ion separation.

2. Project Rationale

2.1 Objectives

- Determine whether β-oriented MFI zeolite membranes were effective and efficient in the separation of NaCl from water and the adsorption of heavy metal ions such as zinc and copper(II) ions.
- Compare its separation capabilities with the α-alumina support structure ceramic membrane

2.2 Hypotheses

- A β-oriented MFI zeolite membrane can be synthesized on a porous zirconium MOF support
- The membrane will be able to adsorb heavy-metal ions and separate NaCl from seawater.
- The effectiveness of the zeolite membrane will be greater than that of the alpha alumina support structure ceramic membrane

2.3 Variables

Independent Variable	The zirconium MOF synthesized on a β-oriented MFI zeolite membrane.
Dependent Variable	The percentage removal of heavy metal ions and aqueous sodium chloride from deionised water through the experimental membrane.
Control	The α-alumina support membrane

3. Materials and Methods

3.1 Materials

3.1.1 Chemicals

- Zirconyl chloride octahydrate
- Tetramethylammonium hydroxide
- Polyvinyl alcohol
- Sodium chloride salt
- Hydrated copper (II) sulfate salt
- Hydrated zinc sulfate salt

3.1.2 Apparatus

- Aluminum oxide tubular microfiltration ceramic membranes
- Biosafety Cabinet
- Oven
- Colorimeter
- Hot Plate
- Sonicator
- Glass bottles
- Arduino chip, servo motor
- Water pumps
- Plastic tubes
- Fish tanks
- Volumetric flask
- Measuring cylinder

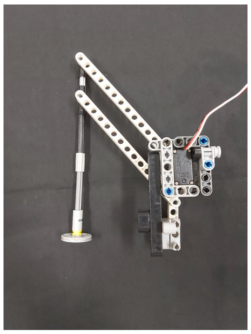
3.2 Methods:

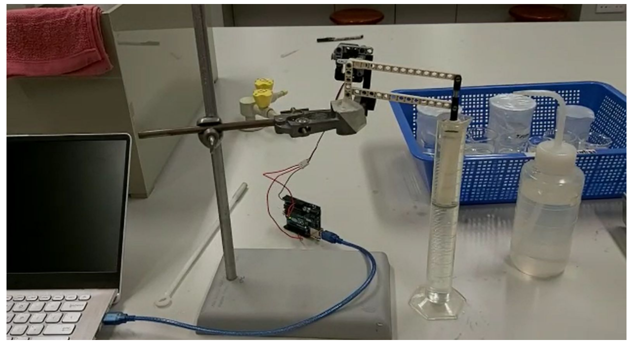
3.2.1 Preparation of Zirconia membrane

1.00 g of zirconyl chloride octahydrate was added to 48.72 cm^3 deionised water and sent to ultrasound treatment for 5 mins to obtain zirconyl chloride octahydrate in aqueous form. 0.557 cm^3 of aqueous tetramethylammonium hydroxide was added dropwise to the solution and was left for 15 mins under ultrasound treatment. The sols were then obtained. The sols were then dried in an oven overnight at 110 degrees celsius. Immediately after, 10% mass concentration of polyvinyl alcohol (PVA, Sigma-Aldrich, >99%) was added to adjust the viscosity of the sols. The colloidal sols were then transferred into a 100 cm^3 measuring cylinder and the aluminium oxide tubular microfiltration membranes were then dip coated. Remove after placing the membrane for 30 seconds in the sol and place the wet membranes in air conditioning for 12 hours before drying in an oven at 110 degrees celsius for 12 hours.

3.2.2 Preparation of dip-coating set-up

As there was no cheap commercial dip coating machine and as the labs did not have such a device, a custom device was programmed and created. An arduino chip was used to control a servo motor mechanism that raised and lowered the α- alumina membrane to carry out dip-coating of the membrane.





3.2.3 Preparation of test solutions

3.5% aqueous sodium chloride solution was prepared by dissolving 35g of sodium chloride NaCl in 1dm^3 of deionised water in a 1dm^3 volumetric flask. 100ppm (~0.04%) of copper(II) ions was prepared from copper(II) sulfate by dissolving 0.393g of copper(II) sulfate in 1dm^3 of deionised water in a 1dm^3 volumetric flask. 100ppm (~0.04%) of zinc ions from zinc sulfate was prepared by dissolving 0.439g of zinc sulfate in 1dm^3 of deionised water in a 1dm^3 volumetric flask.

3.2.4 Preparation of filtration set-up

A set-up that was able to incorporate a tubular ceramic membrane and mostly airtight was designed. The set-up consists of a water pump, 2 mini fish tanks, plastic tubes and finally the membrane itself.

4. Results

4.1 NaCl separation capabilities

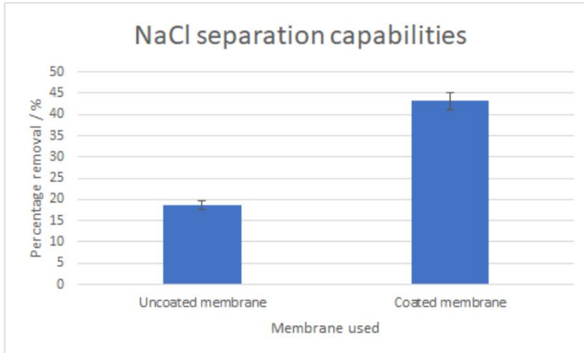
Table showing NaCl separation of α alumina membrane

Replicates	1	2	3	4	5
Concentration of sodium chloride in starting solution/ppt	35.0				
Concentration of sodium chloride in filtrate/ppt	28.5	28.3	27.8	28.5	28.3
Change in Concentration/ppt	-6.54	-6.74	-7.24	-6.50	-6.67
Percentage Removal / %	18.7	19.3	20.7	18.6	19.1

Table showing NaCl separation of zirconium membrane

Replicates	1	2	3	4	5
Concentration of sodium chloride in starting solution/ppt	35.0				
Concentration of sodium chloride in filtrate/ppt	19.5	20.1	19.4	20.4	20.5
Change in Concentration/ppt	-15.5	-14.9	-15.6	-14.6	-14.5
Percentage Removal / %	44.2	42.5	44.6	41.7	41.4

Here were the results of our desalination tests conducted on our test and control membranes. Using the salinity meter, a probe was inserted into the solutions to measure the concentration of NaCl in the test solutions. The first table from the left represents the data collected from 5 different replicates investigating the desalination capabilities of the alpha alumina ceramic membrane. From the first table, the average concentration change of NaCl from the starting solution and the filtrate, when the α alumina ceramic membrane was used, was -6.74 parts per thousand and the average percentage removal of NaCl was 18.7%. Thus, it was observed that the alpha alumina ceramic membrane was not very effective in desalination. The second table from the left represents the data collected from 5 different replicates investigating the desalination capabilities of the zirconium membrane. From the second table, the average concentration change of NaCl from the starting solution and the filtrate, when the zirconium membrane was used, was -15.00 parts per thousand and the average percentage removal of NaCl was 43.1%. Thus, it was observed that the zirconium zeolite membrane was significantly more effective in desalination. The Zirconium membrane showed a clear reduction in the concentration of NaCl after filtration. There was an average percentage concentration removal of 43.1%, 24.4% more than the alpha alumina ceramic membrane. A Mann-Whitney U Test was conducted and it was found that the results were significant as P value was smaller than 0.05. Thus, the Zirconium Zeolite membrane showed great potential in desalination.



The bar chart shows the effectiveness of the alpha alumina support membrane and the zirconium zeolite membrane in desalination. It could be observed that the zirconium zeolite membrane was more than twice as effective as the alpha alumina support membrane in filtering off NaCl from deionised water.

4.2 Heavy metal ions separation

4.2.1 Copper (II) ions separation capabilities

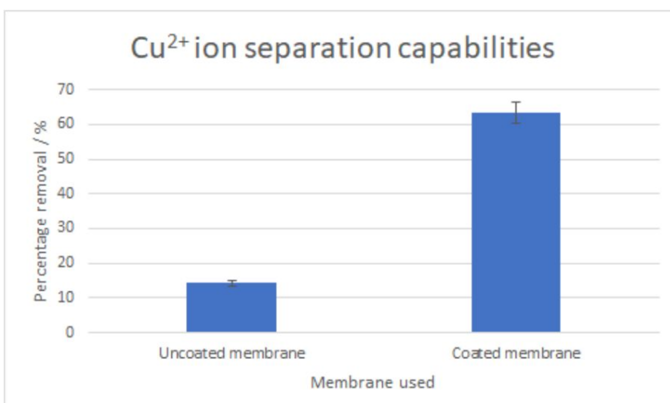
<u>Table showing copper(II) ion separation of α alumina membrane</u>

Replicates	1	2	3	4	5
Concentration of copper(II) ions in starting solution/ppm	100				
Concentration of copper(II) ions in filtrate/ppm	77.1	88.2	87.3	88.6	87.5
Change in Concentration/ppm	-22.9	-11.8	-12.7	-11.4	-12.5
Percentage Removal / %	22.9	11.8	12.7	11.4	12.5

<u>Table showing copper(II) ion separation of zirconium membrane</u>

Replicates	1	2	3	4	5
Concentration of copper(II) ions in starting solution/ppm	100				
Concentration of copper(II) ions in filtrate/ppm	34.2	35.3	38.4	38.0	37.5
Change in Concentration/ppm	-65.8	-64.7	-61.6	-62.0	-62.5
Percentage Removal / %	65.8	64.7	61.6	62.0	62.5

Here were the results of our copper(II) ion separation tests conducted on our test and control membranes. The first table from the left represents the data collected from 5 different replicates investigating the copper(II) ion separation capabilities of the alpha alumina ceramic membrane. From the first table, the average concentration change of copper(II) ions from the starting solution and the filtrate, when the α alumina ceramic membrane was used, was -14.3 milligrams per dm^3 and the average percentage removal of copper(II) ions was 14.3%. Thus, it was observed that the alpha alumina ceramic membrane was not very effective in copper(II) ion separation. The second table from the left represents the data collected from 5 different replicates investigating the copper(II) ion separation capabilities of the Zirconium membrane. From the second table, the average concentration change of copper(II) ions from the starting solution and the filtrate, when the Zirconium membrane was used, was -63.3 milligrams per dm^3 and the average percentage removal of copper(II) ions was 63.3%. Thus, it was observed that the Zirconium membrane was significantly more effective in copper(II) ion separation. The Zirconium membrane showed a clear reduction in the concentration of copper(II) ions after filtration. There was an average percentage concentration removal of 63.3%, 49.0% more than the alpha alumina ceramic membrane. A Mann-Whitney U Test was conducted and it was found that the results were significant as P value was smaller than 0.05. Thus, the Zirconium Zeolite membrane showed great potential in copper(II) ion separation.



This bar chart shows the effectiveness of the alpha alumina support membrane and the zirconium zeolite membrane in copper(II) ion separation. It could be observed that the zirconium zeolite membrane was more than three as effective as the alpha alumina support membrane in filtering off copper(II) ions from deionised water.

4.2.2 Zinc ions separation capabilities

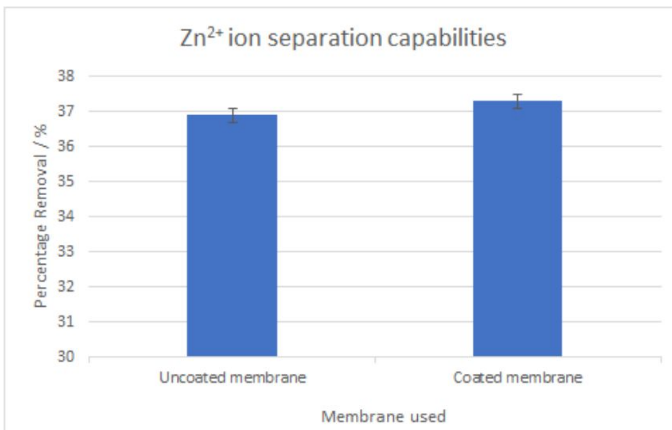
Table showing zinc ion separation of α alumina membrane

Readings	1	2	3
Concentration of zinc ions in starting solution/ppm	100		
Concentration of zinc ions in filtrate/ppm	64.9	62.7	61.9
Change in Concentration/ppm	-35.1	-37.3	-38.1
Percentage Removal / %	35.1	37.3	38.1

Table showing zinc ion separation of zirconium membrane

Readings	1	2	3
Concentration of zinc ions in starting solution/ppm	100		
Concentration of zinc ions in filtrate/ppm	62.2	63.8	62.0
Change in Concentration/ppm	-37.8	-36.2	-38.0
Percentage Removal / %	37.8	36.2	38.0

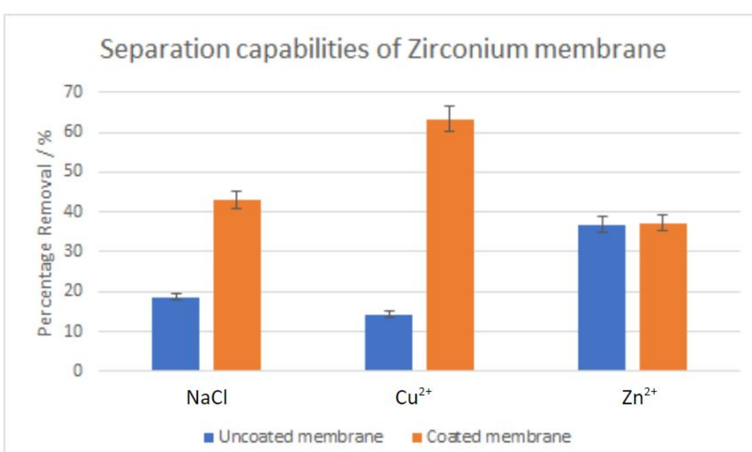
Here were the results of our zinc ion separation tests conducted on our test and control membranes. The first table from the left represents the data collected from 3 different replicates investigating the zinc ion separation capabilities of the alpha alumina ceramic membrane. From the first table, the average concentration change of zinc ions from the starting solution and the filtrate, when the α alumina ceramic membrane was used, was -36.9 milligrams per dm^3 and the average percentage removal of zinc ions was 36.9%. Thus, it was observed that the alpha alumina ceramic membrane was not very effective in zinc ion separation. These were the data collected from 3 different replicates investigating the zinc ion separation capabilities of the Zirconium membrane. From the table, the average concentration change of zinc ions from the starting solution and the filtrate, when the Zirconium membrane was used, was -37.3 milligrams per dm^3 and the average percentage removal of zinc ions was 37.3%. Thus, it was observed that the Zirconium zeolite membrane was rather ineffective in the separation of zinc ions as the percentage removal was way lesser compared to copper(II) ions and NaCl. The Zirconium Zeolite membrane showed a disappointing reduction in the concentration of zinc ions when compared to the control membrane after filtration. There was an average percentage concentration removal of 37.3%, which was only 0.4% more than the alpha alumina ceramic membrane. The results obtained for the separation capabilities of the Zirconium Zeolite, however, were deemed inconclusive. There might be a lot of reasons why the zirconium membrane had failed. Although it had been proven in some research papers on how its separation capabilities were effective when it came to zinc, there might be some errors that occurred when carrying out the testing for its separation capabilities. Some of these errors could include microleaks in the filtration set-up at the joints where the membrane was connected to the tubes, the coating of the membrane being not homogeneous, leaving some parts of the membrane less coated which might allow the zinc ions to pass through without adsorption. Due to these systematic errors as a result of only three replicates conducted, the separation capabilities of zinc ions were inconclusive unless further testing was conducted using multiple new membranes and



newly made set-ups.

This bar chart, with error bars, shows the results of zinc ion separation for the uncoated and coated membrane. The efficiency of the coated membrane was very close to that of the uncoated membrane, showing how the zirconium membrane is ineffective in the separation of zinc ions.

4.3 Overall comparison



The graph shows the overall comparison of the coated and uncoated membranes in terms of the separation of NaCl, copper(II) and zinc ions. There had been an overall trend where the coated membrane had been seen to be consistently more effective in separating harmful copper(II) ions and NaCl from water as compared to the uncoated membrane. Nonetheless, the coated membrane showed a rather disappointing performance when separating zinc ions as mentioned earlier.

5. Conclusion and Future Work

It could be concluded that the zirconium membrane was effective in separating NaCl and copper(II) ions from water, but was rather inconclusive in the separation of zinc ions. Overall, since the percentage removal of the zirconium zeolite membrane for NaCl, copper(II) ions and zinc ions varied only around 50ppm, starting the solution at 100ppm might have been too ambitious. Our starting solution can be at 50ppm instead to attain a higher percentage removal. Moreover, the number of coated membranes in each filtration set-up can attain a greater percentage removal. Set-ups can also be equipped with a higher pressure water pump to increase the rate of cross-flow filtration. Characterisation of the Zirconium zeolite membrane under a SEM can be conducted to measure the pore sizes of the membrane and to inspect the adsorption capabilities of the membrane. More heavy metals ions, such as lead(II) ions, can be tested using the Zirconium Zeolite membrane to ensure that the zirconium membrane is a universal membrane that is effective in absorbing most harmful pollutants from water. Instead of only using the α alumina ceramic membrane as the support membrane, more ceramic membranes can be tested, such as titania ceramic membranes or silicon carbide ceramic membranes. This way, it could ensure that the zirconium coat will be effective on various support structures and not solely on the aluminium support structure. Further collaboration with the American team can be conducted to investigate the carbon dioxide gas separation capabilities of the Zirconium Zeolite membrane.

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